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# Article title: Metallic and plastic dye solar cells


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## Abstract

Dye solar cells (DSC) are quite a new technology in photovoltaics. The traditional DSCs are prepared on conductively coated glass substrates in high temperature using a batch process. Manufacturing the cells on low cost metal and plastic substrates would enable significant cost reductions as well as roll-to-roll mass production. There is a selection of metals and possible conducting coatings for plastics with varying electrical, optical and chemical properties and price. The substrate has a dominant impact on the methods and materials that can be applied to make the cell and consequently on the resulting performance of the device. Furthermore, the substrates influence significantly the stability of the device. The main issue with plastics is their permeability whereas with metals, chemical stability in the electrolyte is the main concern. The leakage of electrolyte and the impact of water intake through the plastics can be affected by the material choices in particular with the electrolyte and dye composition. In the case of the metallic electrodes, the chemical stability can be improved by choosing a corrosion resistant metal, applying a blocking layer or changing to a less aggressive electrolyte. One major focus of the current research of the flexible DSCs is increasing the efficiency by improved low temperature preparation methods and materials especially for the photoelectrode. Another significant challenge is the development of non-corrosive electrolyte and dye combinations that work well even in the presence of significant amounts of water.

Nanostructured dye solar cells (DSC) (Figure 1) are photovoltaic (PV) devices which can be produced from cheap materials using well-known industrial printing and coating methods.[1] A key issue in the commercialization of DSCs is lowering the costs further while maintaining a good efficiency and lifetime. The variables in this equation are the materials and methods used in the manufacturing. Shift from batch processing to roll-to-roll manufacturing is a critical aspect in moving towards mass production.[2] This makes the use of flexible substrates necessary. Moreover, the commonly used transparent conducting oxide (TCO) coated glass substrates are responsible for as much as 60 % of the total material costs of DSC [2,3] and are e.g. 200-times more expensive than aluminium foil.[4]

In addition to this, flexible DSCs widen the range of possible applications. Light weight flexible solar modules make solar energy production possible on large roof-top areas of factories and warehouses that are typically not designed to withstand the weight loads of conventional PV installations. In addition to installation to existing buildings, manufacturing DSCs directly on roofing steel has been a long term goal for many groups working with metallic substrates.[5,6] The flexibly and light weight are desirable properties also for mobile applications and for integration to consumer products. Great potential markets can thus be foreseen for very low cost PV based on metal and plastic substrates, provided that the requirements for efficiency and lifetime can be met. These requirements depend strongly on the application: for instance a good lifetime for PV in mobile gadgets varies typically between 1-5 years in mostly indoor conditions whereas roofing with the integrated PV should last at least for 20 years outdoors. The commercial utilization of flexible DSCs is expected to take place gradually through more and more demanding applications following the development and maturing of the technology.

When DSCs are prepared on flexible substrates, most of the other cell components and their manufacturing methods need to be altered from those used in standard glass based DSCs. Moreover, metals and plastics in the cell introduce new degradation mechanisms that need to be taken care of. In particular the chemical stability of metals and the permeability of plastics that enables material flux to pass through them are important issues. In this regards, the development of flexible DSCs involves significant additional challenges compared to that of the glass based cells.

In this contribution different flexible substrates are discussed and their pros and cons are presented. It is also examined how the substrates affect the materials and methods that can be used in the preparation of the electrodes and the complete cells. Besides examining these preparation aspects and the resulting efficiencies, stability is also reviewed. In particular in reaching long term stability for any commercial applications, the choice of electrolyte as well as the dye to be used with different substrates and the electrodes is shown to be important. The purpose of this study is to look through the whole concept of the flexible DSC to find the currently best solutions for flexible cells as well as the key points for further development.

**OPERATION PRINCIPLE AND DEVICE STRUCTURES**

The typical DSCs are composed of two electrodes that are sandwiched together and filled with liquid electrolyte. The photoelectrode of these devices is typically a porous layer of $TiO_2$ coated with a monolayer of dye on a substrate, conventionally a glass substrate with a transparent conducting oxide (TCO) coating. The dye molecules absorb the incoming photons and inject electrons to the $TiO_2$

conduction band. The injected electrons diffuse through the $TiO_2$ particle network to the conducting substrate and external wiring. Through the external wiring, the electrons are transferred to the counter electrode which consists of a conducting substrate and a catalyst, typically TCO glass coated with platinum. At the counter electrode, the catalyst improves the charge transfer to the electrolyte in which tri-iodide ions reduce to iodide ions. The iodide ions return the charge to the photoelectrode where the dye molecules accept the electron from the iodide and oxidize it back to tri-iodide. Hence, theoretically there should not be any permanent changes in the operation of a DSC. A detailed description of the device physics of DSCs can be found e.g. in our recent review.[7]

As indicated in Figure 1, the DSCs can be prepared on different flexible substrates in three basic configurations: the cell can be made solely on TCO plastics in which case the configuration is similar to the conventional TCO glass based cell with the major exception that the only low temperature processing methods can be used with plastics. The metal can be applied either as the photoelectrode or as the counter electrode substrate. The latter allows the manufacturing of the photoelectrode with high temperature treatments to gain high quality but it suffers from added optical losses as the counter electrode and the bulk electrolyte are shadowing the photoelectrode. When the metal substrate is used at the counter electrode, there are no added optical losses but the flexible photoelectrode needs to be prepared on plastics using low temperature methods.

## FLEXIBLE SUBSTRATES

The present day glass based DSC have been evaluated to cost 2-3 $\$/W_p$ while the threshold for competing with traditional energy sources is considered to be 1 $\$/W_p$.[2,3] Increasing the volume for manufacturing is likely to narrow the gap. But to bridge this gap and in particular if aiming to be much cheaper than alternative PV technologies, significant cost reductions are required. As already mentioned, the latest cost analysis of DSCs revealed that over 60 % of the material costs are due to the TCO coated glass substrates.[2] Therefore using alternative substrates is highly motivating, unless cheaper manufacturing routes for TCO glass are found. Also from the environmental point of view finding alternatives to glass is beneficial: the glass substrates are dominating almost all environmental hazard categories in the life cycle analysis of DSCs, e.g. their share of the global warming effect of DSCs was over 55 %.[8] Plastics and stainless steel have been evaluated to have a lower overall environmental impact compared to TCO glass.[8,9] If the cells are additionally made using low temperature treatments, it would not only lower the processing costs but also decrease the environmental impact of the flexible cells even further.[8-10] Although there are no published cost analyses that would prove the commercial benefits of flexible DSCs apart from the substrate costs, the attractiveness of this technology path can be seen from the fact that numerous companies have chosen R2R production as a strategy to lower manufacturing costs, including G24i, the first commercial manufacturer of DSCs.

The window electrode of a flexible DSC is typically indium tin oxide (ITO) coated plastics such as polyethylene naphthalate (PEN) or polyethylene terephthalate (PET). ITO is, however, costly (Table 1) [2,11] and concerns have been raised that the indium resources could limit the manufacturing at very large scale. The ITO-PEN and ITO-PET have, however, high optical transmittance,[12] sufficient sheet resistance (typically about 15 Ω/sq.), recorded stability in the iodine based electrolyte [13] and they endure a good amount of bending (up to 15 mm radius)[12].

Nanotechnology might provide a solution for making highly transparent and highly conductive substrate. At the moment, the best single-walled carbon nanotube films with about 80 % transmittance reach a sheet resistance of 80 Ω/sq. [14] which is still quite high compared to ITO. The conductivity of an individual nanotube is high and the main factor keeping the conductivity of the nanotube films low is the high contact resistance between the tubes. The preparation of these tubes also requires expensive vacuum process preparation at high temperatures. As carbon can also be used as a catalyst material in DSCs, the conductive layer made from carbon nanotubes when applied at the counter electrode would enhance its performance. Using semi-transparent nanotube films without any additional catalyst is also possible but it is still very much a compromise between electrical performance and transparency.[15] However, at the photoelectrode the carbon nanotube layer would on the other hand increase the leakage current by catalysing the electron transfer to the electrolyte. If transmittance is not required at the counter electrode, which is the case in the completely plastic cell configuration shown in Figure 1, a thick carbon nanotube layer could be used to get a lower sheet resistance. Indeed, it is well known that a thick (60 µm), completely opaque high-temperature sintered carbon powder catalyst layer, instead of nanotubes, can exhibit low enough sheet resistance (5-10 Ω/sq.) to replace the TCO layer as a conductor.[16] It remains as an attractive challenge to achieve the same by low temperature preparations.

Extra fine metal grids are another possibility to replace ITO while reaching low cost and suitability for large area production. It has been claimed that printed metal grids having 80 % transparency can reach 10-times lower sheet resistance compared to a typical TCO coating on glass.[17] Such a decrease in the sheet resistance would improve the cell efficiency by lowering voltage losses. In addition it would enable larger unit cell size which would increase the aperture ratio (active area divided by total area) leading to higher efficiency in the module level. Depending on the grid dimensions, additional transparent coating may be needed to ease the charge transfer.[18] For such a layer even modest conductivity with high transparency would be sufficient as it does not need to carry the current very far but maybe only in about in 100 µm range to reach the metallic grid. The problematic part is that the most common metal inks such as silver corrode very easily in the iodine containing electrolyte.[13] Therefore the use of Nickel has been suggested,[18] but even that has problems in long term stability tests.[19]

The use of a completely metallic substrate is interesting as their sheet resistance is typically three orders of magnitude smaller compared to that of TCO-glass substrates and there are possibilities for major cost reductions as shown in Table 1. Additionally, many metals endure high temperature treatments which are currently still needed to get the highest performing photoelectrodes. However, only expensive metals such as titanium (Table 1) have passed the initial electrolyte soaking tests and even more importantly been stable later on in the long term stability test of complete devices with conventional liquid iodine based electrolyte.[20,21] Stainless steel (StS) was one the cheapest metals to pass electrolyte soaking tests,[5,13] but unfortunately it was recently reported that when the soaking time was extended to 3 months the cheapest grade (304) showed corrosion.[22] Additionally the application of StS to complete DSCs caused stability problems even in much shorter time span (from hours to weeks depending on the case).[20,21,23] The very cheap metals such as aluminium (Table 1, two orders of magnitude cheaper compared to TCO glass)[4] are subject to corrosion when in contact with the conventional iodine containing electrolytes used in DSC.[13,22] Hence, either a protective layer or a non-corrosive electrolyte is needed for those cases. These possibilities are discussed in detail later on.

Woven metal meshes made from very thin metal wires are yet another substrate alternative.[24-28] Typically idea is that the photoelectrode can be prepared around them and thus the conductive layer is in practice not shadowing the photoelectrode at all and additionally the electrolyte can still penetrate the conducting layer.[24] Metallic wires have, however, size limitations and thus the mesh is typically around 100 µm thick. The thickness of the cells is problematic in particular for high viscosity electrolytes such as ionic liquids. There may also be gaps in the electrode between the wires which can reduce the active area significantly.[24] The wires cannot, however, be much thinner as they would otherwise oxidize badly during the high temperature treatments which would reduce the conductivity. There are some other strategies such as weaving extra thin metal and plastic wires together to make a kind of a semi-transparent cloth which is used similar to an ITO plastic substrate.[27]

## PLASTIC ELECTRODES

### Plastic photoelectrodes

The plastic based photoelectrodes need to be prepared using low temperature treatments. Interestingly it is, however, possible to get a high temperature treated $TiO_2$ layer on a plastic electrode using a so-called lift-off method:[31] The idea is that the $TiO_2$ film is deposited on gold-layered glass substrate and sintered at high temperatures. After this the $TiO_2$ layer is detached by dissolving the thin gold layer and the gold is recycled. Then the $TiO_2$ film is transferred to the plastic substrate by pressing. With this method as high as 5.8 % conversion efficiency has been reported and it is still one of highest efficiencies with fully plastic based DSCs as Table 2 indicates.[31]

As mentioned before, employing low temperature methods instead of high temperature ones would reduce both the production costs and the environmental impact of the manufacturing.[8-10] When using low temperature treatments, the bonding of the $TiO_2$ nanoparticles needs to be formed using alternative means to high temperature sintering. Additionally the $TiO_2$ paste should not include organic binders that need to be burned off at high temperatures. It should also be taken into account that FTO glass can resist chemical treatments better compared to ITO plastics. Hence e.g. we have noticed that some acid based low temperature chemical treatments that are suitable for FTO glass substrates cannot be applied for ITO plastics. Nonetheless, there are several different low temperature methods to produce photoelectrodes on plastics: mere $TiO_2$ paste modification,[32,33] pressing,[34-37] UV laser sintering,[38,39] microwave irradiation,[40] electrophoretic deposition,[41] hydrothermal treatments,[42] and changing from $TiO_2$ powder to $TiO_2$ nanotubes.[43] Figure 2 illustrates the evolvement of these methods and the resulting performance.

Miaysaka et al. have reported that optimizing the $TiO_2$ paste and applying only mild heating can result in as high as 5.8 % efficiency.[32] The highest low temperature plastic cell efficiency (7.6 %, Figure 2) has been achieved with the combination of a good low temperature $TiO_2$ paste and some after treatments (pressing and UV-$O_3$).[36] Using pressing with a suitable $TiO_2$ paste composition, Arakawa et al. achieved also the highest efficiency (4.5 %) for a larger area 10x10 cm flexible DSC sub-module.[44] Furthermore, it has been shown that using calendering (i.e. a rolling press) can result in similar efficiencies as static pressing, the former 4.7 % and the latter 5.1 %.[45] The pressing technique, that was originally introduced by Lindström et al., is a very simple, cheap, quick as well as roll-to-roll compatible method to improve the contacts between $TiO_2$ particles.[34]

Another technique that is potentially interesting is the UV laser beam technique. So far the efficiencies of plastic photoelectrodes have been modest,[39] but there are promising initial results shown on $TiO_2$ on glass substrates that confirm that the UV laser beam treatment can be used to get good quality $TiO_2$ films i.e. to get similar efficiencies with the high temperature treatments.[46] The method would likely suit to the roll-to-roll manufacturing of DSC. The control of the UV lasering procedure is challenging from an engineering perspective: the $TiO_2$ layer needs to be locally sintered to form bonding of the $TiO_2$ particles and at the same time the temperature of the plastic underneath the $TiO_2$ film should be kept below 150 °C.

In the preparation of flexible electrodes, besides the substrate also the topping electrode layer needs to flexible. The adhesion of electrode layers e.g. a $TiO_2$ film on the ITO plastics is often problematic and the porous $TiO_2$ films may quite easily detach from the substrate when bending it. This challenge can be overcome by the modification of the $TiO_2$ paste.[32,47,48] Alternatively/additionally the contact with the substrate can be improved by using a separately prepared thin compact $TiO_2$ on the ITO plastic to which the porous $TiO_2$ layer is easier to attach to.[31,37]

As the electron collection is the main challenge in the low temperature prepared $TiO_2$ films, in principle improved light absorption would allows thinner films and a shorter distance for the electrons to travel, thus reaching higher collection efficiency. Currently there is a lot of activity to find highly light absorbing dyes in the DSC field and they have been successfully applied also in plastic cells as shown in Table 2.[49] Another recent trend in DSCs is the co-sensitization of photoelectrodes which may lead to getting better photocurrents overall. Also co-sensitization has been already demonstrated for plastic cells and those first results indicate some improvement in the cell performance.[50] Interestingly however, almost all of the current champion cells including majority of those listed Table 2 are still made with di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) dye better known as N-719 which was developed about 20 years ago.

**Plastic based counter electrodes**

The key characteristics of a flexible counter electrode are good catalytic activity, low cost, easy manufacturing, sufficient adhesion of the catalyst to the substrate, flexibility of both substrate and the catalyst layer, and good overall stability. When using a metal based photoelectrode (see Figure 1) or aiming for a semi-transparent cell, high transmittance of the counter electrode is also a necessary feature.

here are several methods to apply platinum in low temperatures to get a semi-transparent layer. For For instance chemical platinization,[51,52] electrochemical platinization [53] and sputtered platinum [54] have been employed in conjunction with metal based photoelectrodes. The detailed comparison of these counter electrodes is not, however, straightforward as their performance often merely contributes to the fill factor along with many other factors and no specific data of the counter electrodes (e.g. charge transfer resistance, optical transmittance) is typically shown in publications. There are also some other methods of Pt deposition in addition to the previously mentioned ones. For instance, a screen printable low temperature Pt paste has been introduced to make the manufacturing easy and roll to roll applicable.[55] However, in that case the chemical and thermal

treatments that follow the screen printing of Pt were quite long (several hours) and need to be made much shorter for fast roll-to-roll production.

To lower the cost, the use of porous carbon layers has been suggested to replace Pt. However, as the amount of platinum used at the counter electrode is only very small, its costs play only a relatively small role in the total costs of DSCs.[3] Using carbon instead of platinum might be more advantageous mainly from the manufacturing point of view: porous carbon catalyst layers can be applied using quick roll-to-roll suitable methods such as screen printing and pressing. Since carbon is not as efficient catalyst as platinum, a thicker and porous layer of carbon is needed to increase the catalytically active area to compensate for the lower activity. As a result the good carbon powder layers are completely opaque. Just like in the case of porous $TiO_2$ layer, a good contact between the particles is important also in the case of porous carbon layer, and pressing which is used also for $TiO_2$ layers is a good method to achieve this.[56,57] Another similarity between thick porous carbon layers and $TiO_2$ layers is the difficulty to get good adherence with the ITO plastic substrate.[57] Similar to the photoelectrodes, the solution can be found from the modification of the paste: for instance the use of a carbon gel paste combined with pressing has been shown to give good results in terms of flexibility of catalyst layer without affecting the catalytic performance.[58] The use of carbon catalyst layer could actually reduce even the total material costs significantly if the layer had so high conductivity that the ITO coating could be omitted. As already mentioned, that well conducting carbon powder layers have not been demonstrated with low temperature preparation, but only with high temperature sintering.[16] The use of carbon nanotubes as such or as a composite with e.g. carbon powder could be a commercially interesting solution. There are already several different kinds of carbon nanostructures and composites that can be used at the counter electrode and a thorough investigation of those has been presented by Aitola et al.[59]

Besides platinum and carbon catalysts, there is also a third category of catalyst: polymers. Some polymer films such as a thin spin-coated p-toluenesulfonate doped poly(3,4-ethylenedioxythiophene) (PEDOT-TsO) have even such a high transmittance that they can be used with reverse illumination.[60] There are also printable composite pastes of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS), $TiO_2$ and ITO giving 4.38 % efficiency.[61] The idea of the composite paste is to get a mesoporous structure which essentially increases the amount of active area (c.f. porous carbon catalyst layer) as a single PEDOT-PSS coating is not catalytic enough.[60,61] The same approach to increase the active area has also been applied with other conducting polymers such as poly(3,3-diethyl-3,4-dihydro-2H-thieno-[3,4-b][1,4]dioxepine) (PProDOT-$Et_2$) to get an even higher efficiency flexible DSC (5.20 %) than that with a sputtered Pt layer (5.11 %).[62]

**STABILITY ISSUES RELATED TO PLASTICS**

Unlike the glass and metal substrates, the plastic ones are more affected by weathering effects such as humidity and UV irradiation. The permeability of plastic substrates allows water intake as well as enables leakage of electrolyte. There are also mechanical stability issues, namely adhesion and flexibility that affect the plastic electrodes. Due to all these factors depicted in Figure 3, it is not as easy to get good stability with plastics and thus the number of publications reporting the stability of plastic based devices is very small. At the moment the current state of the art in the stability of

plastic DSCs is maintaining efficiency of 2 % for 200 h in high 95 % humidity [63] and for 1000 h in 1 Sun 60 °C.[64]

**Permeability to water**

The effect of water on the cell performance has been debated much recently. It has been shown by Kitamura et al. that the stability of DSCs with the conventional hydrophilic N-719 dye is significantly affected by the air humidity during the cell assembly: even as low as 5-10 % air humidity during cell preparation results in a 20 % loss of photocurrent in 1 month whilst having lower than 0.1 % relative humidity leads to a slight improvement of the photocurrent.[65] These results were measured with glass based cells. In the case of plastics, the effect of water would not be restricted to the assembly but there would be a continuous flux of moisture into the cell through the substrate making the stability issue even greater.

Although the N-719 dye reaches constantly the highest efficiencies and stabilities in glass based devices and it is thus very interesting from commercial point of view, its hydrophilic nature is an issue for plastic based cells. In plastic devices, hydrophobic dyes such as cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II) (known as Z-907) are expected to be much better from the stability point of view as they should be less affected by water. It has in fact been shown that even introduction of large quantities of water (up to 40 %) did not significantly change the performance of the cell when using a hydrophobic organic TG6 dye (i.e. cis-bis(thiocyanato)(2,2′-bipyridyl-4,4′-dicarboxylato){4,4′-bis[2-(4-hexylsulfanylphenyl)vinyl]-2,2′-bipyridine}ruthenium(II) mono(tetrabutylammonium) salt).[67] Interestingly in that case having 20 % water in the electrolyte actually improved the photocurrent with about 5 % compared to having no water at all.[67] Furthermore, a cell with 20 % water in the electrolyte was reported to be stable in a 750 h light soaking test.[67] Similarly, the performance of DSC using ionic liquid electrolytes has been shown to improve by increasing the amount of water in the electrolyte.[68] It shows that a certain amount of water can even be good for the DSC performance and stability.[69] As the annual amount of water up take through a low cost water penetration blocking layer has been estimated to be 10 %,[67,70] the lifetime of such cells should from the water penetration point of view be some years. This is already a sufficient lifetime from perspective of many portable applications (e.g. electronic gadgets).

In addition, Lee et al. have demonstrated that changing from N-719 dye to a heteroleptic ruthenium complex dye (SJW-E1) the stability of a plastic cell could be significantly improved in a 500 h 1 Sun light soaking test.[49] They suggested that the improvement was due to the amphiphilic properties of the SJW-E1 dye which would prevent desorption of the dye by water molecules.[49]

These good stability results with significant amounts of water are important also for glass based cells as they imply that moisture in the preparation phase would not cause significant problems when using suitable dyes. It could be a significant benefit in regard of manufacturing to at least partially relax the stringent moisture regulation requirements suggested by the results of Kitamura et al.[63]

**Permeability and leakage of electrolyte components**

Besides water penetration through the porous plastic substrates, there may also be leakage of electrolyte out of the cell. The application of non-volatile ionic liquids is one way to keep the

electrolyte solvent from leaking out of the cell. Ionic-liquids have, however, high viscosity and thus the charge transfer in the electrolyte is more sluggish compared to organic liquid electrolytes. Hence with ionic liquids, the concentration of the redox pair needs to be increased and the distance between the electrodes needs to be minimized. Using dyes with high extinction coefficients that allow the use of a thinner photoelectrode has proven to be a good strategy to make the cell thinner and improve its performance: for instance a fairly new dye, C101 (NaRu(4,4′-bis(5-hexylthiophen-2-yl)-2,2′-bipyridine)(4-carboxylic acid-4′-carboxylate-2,2′-bipyridine)$(NCS)_2$), has a high molar extinction coefficient and it gives over 9 % efficiency with ionic liquids and maintains that performance in 1000 h 60 °C 1 Sun light soaking test.[71]

Besides the solvent evaporation, the leakage of other electrolyte components such as iodine and 4-tert-butylpyridene should be prevented as well. A combination of solely non-volatile materials including ionic liquid, carbon black and polyaniline (i.e. no added iodine or tBP) has been suggested to solve this problem.[72] With this radical apparently iodine free electrolyte, Lee et al. got as high as 5.81 % efficiency and good stability in 1000 h at 70 °C aging test in a glass based DSC.[72] Later on it has been, however, shown that ionic liquids do actually contain residues of iodine which contribute significantly to the cell performance.[73] This kind of electrolyte may thus not be immune to the escape of iodine from the cell.

One way to avoid the leakage problem is to use completely solid electrolytes that do not contain the iodide/tri-iodide redox couple. Among such electrolytes the best performing ones are spiro-MeOTAD with highest reported efficiency of 5.1 % [74] and poly(3,4-ethylenedioxythiophene) (PEDOT) with 6.1 %.[75] One main issue related to solid electrolytes is their penetration into the $TiO_2$ film. Spiro-MeOTAD has comparatively good wettability due to its relatively small size among the solid hole conductors. But even so it is easier to get a better filling percentage to a thin $TiO_2$ layer and thus the current optimum thickness of the $TiO_2$ film is only 2 μm.[74] There has been a recent development in regard of manufacturability: it was shown that spiro-MeOTAD can be screen printed on the photoelectrode which is a significant advantage compared to previously used spin-coating which is suitable only for batch production and causes large material losses.[76] In the case of PEDOT, the best results have been gained using in-situ polymerization.[75] The solid electrolyte cells also benefit from highly absorbing dyes and are typically subject to increased optical losses as the hole conductors absorb light. Another typical issue is the increase of recombination losses and thus a blocking layer may be needed. Hague et al. have demonstrated the use of a solid electrolyte accompanied by an $Al_2O_3$ blocking layer on the photoelectrode in completely flexible device having 2.5 % efficiency at 1 Sun and as high as 5.2 % efficiency at 0.1 Sun.[77] No stability data of solid electrolytes has been presented so far which implies that further work is needed in that regard.

**UV sensitivity of plastics**

Unlike glass and metal substrate, plastics, in particular ITO-PEN, suffer from long term UV irradiation.[78] The visible yellowing of the plastic due to UV light exposure has been related to the reactions of naphthalene dicarboxylate that is used in ITO-PEN.[78] Since ITO-PET does not contain that ingredient, it has been found to be much more stable.[78] The active components of DSCs degrade also under UV irradiation causing visible bleaching of the electrolyte.[79] Hence, currently UV blocking layer is anyway needed on the DSCs and that protects at the same time the UV sensitive plastic substrates.

## METALLIC ELECTRODES

Metallic electrodes can be used either at the photoelectrode or the counter electrode and both configurations have their own benefits (Figure 1) as will be discussed in more detail later on. Before going to the details of different electrode types it is interesting to note that there is a major difference between the two different cases from the stability perspective: For instance the StS based metal photoelectrodes and counter electrodes have a very different degradation patters and even the visible changes are very different.[20,21,23] Moreover some metals such as Inconel have been stable at the photoelectrode but highly unstable at the counter electrode and vice versa as shown in Table 3.[20,21] These findings suggest that the degradation mechanisms in those two cases are in fact different. The main reason for this is assumed to be the potential difference between the electrolyte and the electrode which is opposite in the case of photoelectrodes and counter electrodes.[20,21] The potential is again known to affect significantly e.g. corrosion reactions. In working conditions, the photoelectrodes is more protected from corrosion whereas the counter electrode is more prone to corrosion.

### Metal based photoelectrodes

The main reason why metals have been applied at the photoelectrode is that they enable the high temperature sintering of the porous $TiO_2$ layer and thus it is much easier to get a high quality photoelectrode than in the case of plastic substrate. In fact, the highest flexible cell efficiency (8.6 %) has been achieved with a metal based photoelectrode as can be seen from Table 2.[51] Additionally, the metal based photoelectrodes endure bending very well (see Figure 4).[52] The metals show also clear potential for fast roll-to-roll production as even the sintering of the $TiO_2$ film can be reduced from the typical 30 min to 12.5 s without any loss in the cell performance when ultra fast near infra red sintering is used instead of normal heating in an oven.[80]

There is a lot of scatter in the initial performance data of the stainless steel based cells: the best efficiencies are not much lower compared to glass cells illuminated reverse side [81] and the worst are almost 90 % lower compared to FTO glass/titanium references.[82] It seems likely that this deviation originates from the very quick degradation of stainless steel based photoelectrodes under working conditions.[20] Hence even the varying amount of light that the cells have been exposed to prior to their initial measurements can significantly influence their initial measured performance. This fact describes also very well the severity of the degradation problem of StS based photoelectrodes.

The cause of the quick degradation of StS photoelectrodes is still not completely understood: Firstly, it is generally thought that corrosion might be an issue (as it is in the case of StS counter electrodes [21,23]), but detailed analysis did not show any signs of corrosion e.g. no clear change in electrolyte colour and no pit holes on the substrate.[20,83] Furthermore using metals with improved corrosion resistivity e.g. acid proof steel instead of stainless steel did not improve the stability either (Table 3).[20] In addition, as mentioned earlier the polarization of the photoelectrode should protect from corrosion in the case of photoelectrode. Secondly, increased leakage current from the StS electrode has been hypothesized,[52] but the recombination via StS substrate was actually proven to be lesser compared to FTO glass.[81] Thirdly, contamination of the $TiO_2$ layer by harmful metal oxides can reduce cell performance,[84] but yet again no contamination has been detected.[81,83]

In order to find stable options for metal based photoelectrodes, several different kinds of metals at the photoelectrode were tested.[20] To date, only Inconel alloy and titanium (Ti) based photoelectrodes have passed 1000 h in a 1 Sun light soaking.[20] Ti showed better initial performance compared to Inconel as there was an additional resistance between the dyed $TiO_2$ layer and the Inconel substrate reducing the fill factor in the Inconel cells.[20] Ti has also very low recombination current as its surface is covered by titanium oxides and thus the performance should be good even in low light conditions.[37,85,86] Treatments of the Ti metal substrate surface such as polishing have been shown to improve the photocurrent to some extent.[87] Contrary to this in another study of metal based photoelectrodes, making the surface of the metal rougher resulted in some improvements in the photocurrent.[88] The major down side of Ti foil is its cost as illustrated in Table 1. Additionally, it was recently discovered that the resistivity of the Ti substrate increases as much as 1-2 orders of magnitude in high temperatures (450-500 °C) unlike that of StS substrate.[12] This does not affect the performance at small scale as the conductivity is even with such a decrease still superior compared to TCO coatings. However, in very large sized modules additional current collectors might be needed on the metal side as well or at least this needs to be taken into account in the design of the cell geometry.

Instead of using expensive and intrinsically stable metals, another alternative is the use of blocking layers on cheaper metals. The initial performance of StS with additional coatings has been excellent.[51,52] It was, however, shown that at least a thin (up to 35 nm thick) compact atomic layer deposited $TiO_2$ layer on top of StS substrates did not have any effect on aging.[89] This further implies that the cause of the degradation is not typical corrosion and the stabilization of StS based photoelectrodes is particularly difficult to accomplish. It might be that the application of multiple layers such as in literature [6,51,52] might be sufficient to stabilize the device. Further studies on the topic are, however, needed.

**Metal based counter electrodes**

In the case of metal based counter electrode, using low temperature methods such as sputtering in the preparation of the catalyst layer has in general been a much better option compared to high temperature treatments.[13,21] This has been thought to be caused by the increased oxidation of the metal surface in high temperatures which would hinder the change transfer. However, the selection of viable deposition methods for a catalyst in the case of metals is larger than with plastics; for instance some chemical deposition methods that dissolve ITO work well with metals.[90] Also carbon based counter electrodes suit very well with StS substrates and in such a case as high as 9.15 % efficiency has been reached.[91]

There are some differences in the performance of different metal based counter electrodes when using the similar catalyst layers.[5,13,21,90] It seems likely that those differences may also arise from the differences in the oxide layers.

Unlike in the case of metal based photoelectrodes, the typical degradation path way is very clear with metal based counter electrodes: the degraded metal CE cells show visible loss of electrolyte colour which is typical for a chemical reaction of iodine, there are clear corrosion pit holes in the metal substrates in the SEM images as well as build up of apparent corrosion products [21,23]. As there was corrosion in the case of StS 304 substrate, the next step was to move towards more corrosion resistant metals.[21] Using acid proof steels and Ti improved the stability compared to stainless steels

as shown in Table 3 but only Ti reached consistently good stability.[21] Another viable substrate option for a counter electrode from the stability point of view could be graphite sheets, but that still needs to be verified. A graphite sheet topped with a porous carbon layer has been shown to give a good electrical performance.[92]

To reduce the cost of the substrate, a blocking layer on the metal counter electrode has also been investigated. The application of a thin (20 nm) sputtered Pt layer on the metal stabilized the cell in the case of most studied metals such as StS 304 (Table 3).[21] It appears that if the metal is very prone towards corrosion (e.g. Inconel alloy) even such a layer is not sufficient to stabilize the cell.[21] Hence it seems likely that cheaper metals than StS that corroded already in the electrolyte soaking test would not be stable enough with such a blocking layer. Thus to widen the selection to much cheaper metals and to reach intrinsic stability, a non-corrosive electrolyte is needed.

**NON-CORROSIVE ELECTROLYTES**

If very cheap metal films and plastics with printed metal grids were use as substrates, the proposed metallic structures would enable a much larger unit cell size due to a significantly lower sheet resistance (<10 times lower). This allows an increase in the proportion of the active area, i.e. the aperture ratio, leading to a higher efficiency in the module level.

It needs to be determined which alternative substrate – electrolyte combinations are stable as such. Interestingly enough, even though many alternative redox couples have been presented and named 'non-corrosive'. No stability data of metals or metal based cells with those electrolytes have been presented so far. Moreover, no cells were actually even prepared on metallic substrates except for one study.[93] As iodine is known to be highly corrosive, it is very likely that these alternative electrolytes are less corrosive than the iodine containing ones. However, it does not prove that the easily corroding metals such as copper would be stable in these alternative electrolytes.

The application of the alternative electrolytes affects not only the corrosiveness but also the charge transfer characteristics. One typical issue with the alternative redox couples is that the charge recombination is faster and thus the electron lifetime is shorter compared to the iodine based electrolytes. This matter has been previously addressed by applying a nano blocking layer of $Al_2O_3$ on the $TiO_2$ film.[94,95] The application of such a film, however, adds steps in the manufacturing process and depending on the deposition method it can also be expensive. Recently, it was reported that certain types of organic dyes can be used without blocking layers to get as high as 6.7 % efficiency.[96] Others have also appreciated the use of large dye molecules with bulky cobalt complex redox couples to get good results.[97,98] Another benefit of using large sized cobalt complexes is that they might have a slower penetration through plastics compared to the smaller sized iodide and tri-iodide, but this needs to be still proven.

Other interesting redox couples are disulfide/thiolate redox couple which have achieved 6.4 % efficiency [99] and tetramethylthiourea / tetramethylformaminium disulfide dication giving 3.1 %.[93] The particularly interesting point with the latter one is that it has been used together with aluminium based counter electrodes.[93] Li et al. also found that the selection of the counter electrode catalyst is also very important and in their study they got much better results with a carbon catalyst layer than with a conventional platinum layer.[93]

**TECHNOLOGY OF FLEXIBLE DYE SOLAR CELLS**

The flexible DSC technology has evolved from the initial proofs of concept [100] to over 8 % [51] during the past 10 years. Figure 5 shows the major improvements in the performance, stability and up-scaling that occurred during this time. The large scale manufacturing of DSCs and the pathways to reach that was the main focus in our other recent review [4] and thus in this contribution only the key factors are presented.

The flexible cells have significant commercial interest, for instance G24i is already manufacturing flexible cells with a metallic electrode. Their product has a Titanium foil as the photoelectrode substrate and a plastic based counter electrode.[101] Their DSC 14 cm x 20 cm modules give approximately 2 % efficiency.[101]

The flexible DSCs have some differences in the up-scaling compared to glass based cell even beyond the roll-to-roll manufacturability. Firstly, a metal based cell needs to be physically cut and separated to form a series connection (c.f. in the case of TCO glass and plastics, only the TCO can be cut not the whole substrate to electrically isolate different sections). A larger module can be formed e.g. by laminating the metal strip cells next to each other as done in the design that G24i uses.[101] Secondly, the metallic substrates are so highly conducting that they do not usually require any further current collector grid. Thirdly, low temperature laminating materials need to be employed due to the temperature restrictions of the plastics. This affects the selection of available laminating and sealing materials.

Another significant cost, time and environmental factor in the preparation of conventional DSCs are the high temperature treatments. [8-10] Hence, having the cell made altogether (including metallic electrodes) in low temperatures is one aim as suggested in our earlier work.[4] The metallic counter electrodes prepared in low temperatures exceed already the performance of the high temperature treated ones. [13,21] Contrary to this, the major benefit of metallic photoelectrode substrates i.e. the suitability for high temperature treatments would not be significant anymore, but there would still be the larger optical losses compared to plastic based photoelectrodes. Thus, plastic photoelectrodes might be more interesting in the long run. In the case of counter electrodes, the metals have the upper hand compared to plastics in a non-corrosive electrolyte: metals are highly conducting, non-permeable, and some of them are very cheap.[4] Having said this, the suitability and optimum choice of the flexible substrate materials is not a fixed question, but it needs to be tested whenever new materials, e.g. alternative redox couples, non-volatile solvents, as well as different manufacturing methods are developed.

Based on these current trends we can envision that the future flexible DSC would have a plastic based photoelectrode with e.g. printed metal grid as TCO coating instead of ITO. The replacement of ITO coatings is a pursuit in many fields not just in DSCs. The dye would be stable in water and act as a blocking layer between $TiO_2$ and the electrolyte. The electrolyte would be either non-corrosive liquid electrolyte with alternative redox couple or completely solid state one. The liquid electrolyte maybe transformed into a semi-solid form to improve the mechanical stability and it would be printed in the cell instead of pumped. The counter electrode would be made on very low cost metal such as aluminium and catalyst layer would be e.g. low temperature printed carbon. In our recent publication, we have presented a schematics for production for DSCs incorporating similar visions.[4] As mentioned in the beginning, the conducting glass substrates are the dominant cost factor among

the material costs [2,3] and using for instance aluminium instead of FTO coated glass would take the costs of the substrate to a mere fraction.[4]

## Conclusion

The application of metals and plastics in dye solar cells is favourable due to their suitability to roll to roll mass production, possible cost reduction and increase in the number of potential applications. Although there have been major improvements in the performance of flexible cells over the past ten years, the efficiencies of flexible cells are still not as high as with the traditional glass based cells. In particular the low temperature methods used for the preparation of photoelectrodes are an important area for further development. Besides improving the connections between the $TiO_2$ particles of the photoelectrode film, development of dye (higher absorption, higher blocking) may play an important role. Another main issue with the flexible cells is the stability. The permeability of plastics enables both the leakage of the electrolyte as well as the penetration of water into to the cell which may degrade the performance of DSC over time. The metals on the other hand have issues in regard of chemical stability: most metals corrode in the traditional iodine based electrolyte. The stability of the metals is important also from the view of plastics based cell as extremely finely printed metal grids are interesting alternatives to expensive and resource limited ITO coatings for plastic electrodes.

Improving the intrinsic stability of the flexible DSCs is actually mostly related to the development of the electrolyte, i.e. reducing its corrosiveness and tendency to leak, and the dye, i.e. making it less affected by water and improving suitability with new electrolytes. Significant advancements have been recently made in the field of alternative redox couples and in particular cobalt complex electrolytes have been giving very high efficiencies. In addition, some bulky dyes have been found that work very well with cobalt electrolyte even without additional blocking layers on the $TiO_2$ film. It also needs to be clarified which metals are stable in these new electrolytes. There may be possibilities to use substantially lower cost metals such as aluminium which was investigated very recently. In regards of penetration of water, there are already now some dyes which give good performance even if there are significant amounts of water in the electrolyte.

Momentarily these aspects, e.g. corrosiveness and effect of water, are often viewed only separately and in the future more comprehensive view needs to be taken in the materials development i.e. achieving the different criteria simultaneously. The three main challenges in our view are: Firstly, a flexible photoelectrode that works well with a non-corrosive electrolyte. This is much more complicated than it seems due to the fact that electron collection is a major issue with both low temperature photoelectrodes and alternative redox couple even separately. Moreover, even though a blocking layer may not be needed on the porous $TiO_2$ film, such is still currently required on the photoelectrode substrate and most of the methods used for the glass substrates are not applicable for plastics. Secondly, the stability of alternative electrolytes and new dyes need to be improved in general. Thirdly, the dye and electrolyte combination need to be simultaneously non-corrosive, durable against water and non-volatile.

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## Figure captions

Figure 1. Structure of different flexible cells and their major pros and cons. The image is not in scale. Photoelectrode = PE, counter electrode = CE, transparent conductive oxide = TCO.

Figure 2. State of the art efficiency for different methods to prepare $TiO_2$ photoelectrodes on plastic substrates and when it was achieved. The efficiency records of plastic photoelectrodes (some with the same technique) are marked with red diamonds and the logarithmic trend line is based on those. The methods resulting low efficiencies and reports on minor improvements were left out.

Figure 3. Illustration of stability issues affecting a plastic based electrode.

Figure 4. Demonstration cell made with photoelectrode on StS and counter electrode on ITO-PET showing pattering possibilities as well as good flexibility.

Figure 5. Development of flexible electrodes for DSCs on a rough time line. The initial flexible DSCs were completely on plastics and the development of those is described by the lowest branch. The metal based counter electrodes were introduced next and that cell structure is shown by the middle branch. After that the concept of metal based photoelectrodes was developed and that is described by the highest branch. The most important developments are with bold font. The light gray dashed line and the light gray texts represent objectives and possible developments of the future.

## Tables

Table 1. The characteristics of different substrates for DSCs. The list includes sheet resistance, optical transmittance, stability when soaked in conventional iodine containing electrolyte and cost. The estimated costs are provided for a rough comparison between the materials, and do not represent the actual prices available to a manufacturer at any specific time or conditions.

| substrate type | Sheet resistance Ω/sq. | Transmittance at 550 nm | Iodine electrolyte soaking | Estimated cost ($/m$^2$) |
|---|---|---|---|---|
| FTO glass | 15 | 83 % | Pass | 12-40 [2,25] |
| ITO-PEN | 15 | 85 % [12] | Pass [13] | 8-72 [2,11] |
| carbon nanotubes on plastic/glass | 80 [14] | >80 % [14] | | |
| carbon powder on glass | 5-10 [16] | Opaque | Pass [30] | |
| printed Nickel grid | 0.28 [18] | 66 % [18] | Fail [19] | |
| Titanium sheet | | Opaque | Pass [20-21] | 12-90 [4,25] |
| Molybdenum sheet | | Opaque | Pass [22] | |
| Stainless steel 316 sheet | | Opaque | Pass [22] | |
| Stainless steel 304 sheet | 0.0038 [13] | Opaque | Pass [5,13,19], Fail [22] | 4 [29] |
| Steel sheet (various types) | | Opaque | Fail [5] | |
| Copper sheet | 0.00009 [13] | Opaque | Fail [13] | |
| Aluminium sheet | 0.00019 [13] | Opaque | Fail [13,22] | 0.05 [4] |
| Zinc sheet/coating | | Opaque | Fail [5,22] | |
| Iron sheet | | Opaque | Fail [22] | |
| Titanium mesh | | | Pass [20-22] | 15-20 [25] |

Table 2. The best photovoltaic performance of cells when having photoelectrode and/or counter electrode prepared on flexible substrates in comparison with completely glass based cell. HT = high temperature, LT = low temperature.

| PE | CE | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (mV) | *FF* | *H* (%) | *Ref.* |
|---|---|---|---|---|---|---|
| HT $TiO_2$ on FTO glass | Pt sputtered FTO glass | 17.73 | 846 | 0.75 | 11.18 | [66] |
| HT $TiO_2$ on FTO glass | HT carbon on StS | 16.8 | 790 | 0.685 | 9.1 | [91] |
| HT $TiO_2$ on FTO glass | Chemical Pt on Ni | 15.32 | 710 | 0.71 | 7.29 | [90] |
| HT $TiO_2$ on FTO glass | Carbon on graphite | 13.1 | 703 | 0.702 | 6.46 | [92] |
| HT $TiO_2$ on FTO glass | Sputtered Pt on StS | 12.4 | 703 | 0.6 | 5.24 | [13] |
| HT $TiO_2$ on StS with multiple blocking layers | Chemical deposition of Pt on ITO-PEN | - | - | - | 8.6 | [51] |
| HT $TiO_2$ on Ti | Electrochemical deposition of Pt on ITO-PEN | 13.6 | 780 | 0.68 | 7.2 | [53] |
| LT pressed and UV-$O_3$ treated $TiO_2$ on ITO-PEN | Pt sputtered on ITO-PEN | 14.98 | 732 | 0.692 | 7.6 | [36] |
| LT $TiO_2$ with highly absorbing dye on ITO-PEN | HT platinized FTO glass | 12.69 | 741 | 0.671 | 6.31 | [49] |
| HT $TiO_2$ on ITO-PET with lift-off method | Pt on ITO-PET | - | - | - | 5.8 | [31] |
| LT $TiO_2$ on ITO-PEN | HT platinized FTO glass | 11.99 | 752 | 0.645 | 5.8 | [32] |
| LT $TiO_2$ on ITO-PEN | PProDOT-Et2 on ITO-PEN | 11.22 | 740 | 0.63 | 5.20 | [62] |

Table 3. Stability of different metals used as such as photoelectrode [20] and counter electrode [21] substrates in complete DSCs under 1 Sun equivalent light intensity at 40 °C for 1000 h test. Stable = passing of 1000 h with only minor loss of performance; unstable = major loss of performance during 1000 h test; very unstable = major loss of performance in the first 24 h of testing.

| | Photoelectrode [20] | Counter electrode without a blocking layer [21] | Counter electrode with a sputtered Pt blocking layer [21] |
|---|---|---|---|
| StS 304 | very unstable | very unstable | stable |
| StS 321 | very unstable | very unstable | stable |
| Acid proof steel 316 | very unstable | unstable | stable |
| Acid proof steel 316L | very unstable | unstable | stable |
| Inconel 600 | stable | very unstable | unstable |
| Titanium | stable | stable | stable |

## Related Articles

| Article ID [or Subtopic] | Article title |
|---|---|
| WENE-027 | Dye-sensitized solar cells |
| WENE-292 | Dye-sensitized solar cells |
| | |